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Exhibit 16



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There are several approaches available for deposition of insulating films, and a number of means for arc control in such processes. In addition to the classical direct sputtering of insulating targets by the use of radio-frequency power, reactive sputtering using direct-current power has been frequently used because of its higher rate of deposition, and several processes and equipment configurations have been devised for this purpose. These include simple dc sputtering from a single target; single-target sputtering using dc plus an alternating voltage component, either pulsed or sinusoidal; dual-cathode sputtering using sinusoidal power; and new techniques using pulsed power and dual cathodes. This paper will describe the methods used or proposed for dc reactive sputtering and the equipment, physical principles, and operating features of each.`

DC SPUTTERING -- CONTROLLING ARC ENERGY

Except for a few high-power industrial processes, switchmode dc power supplies have come to dominate the plasma sputtering power market. This has occurred because of the intrinsic positive features of this topology as compared to the formerly-used thyristor types. These features result from the basic nature of the switchmode topology, shown in Figure 1 on page 6.

The Switchmode Supply

The supply outlined in Figure 1 is a single-phase pulsewidth-modulated (PWM) design; most commercial units on the market today utilize this approach. In this design, the mains voltage is rectified to produce an uncontrolled dc voltage by the ac-dc converter (C), which is delivered to the switch element (S). The switch element is the heart of the power supply; it produces a controlled alternating voltage from its uncontrolled dc input and applies this voltage to the primary of transformer (T). The transformer is used not only to provide isolation from the mains, but also to move the output voltage and current to the levels required by the load. The output of the transformer is applied to a rectifier (R), which produces a dc output with ripple at the switching frequency. This ripple is reduced by L-C filter (F). The other elements shown in Figure 1 will be described later.

Advantages of the Approach

The three principal advantages of the switchmode topology all derive from the high frequency of the alternating voltage created by the switch element (S). First, the transformer (T) can be made smaller and lighter for a given power by the ratio of the mains frequency to the switching frequency. For a switching frequency of 50 kHz, this ratio is 1000:1. In actual practice the transformer cannot be shrunk by quite this much because of the insulation and because available magnetic materials at the higher frequencies saturate sooner than the steel alloys used in mains transformers. Nevertheless, it is possible to make a

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transformer capable of handling 10,000 watts that one can easily hold in one's hand. Second, the energy stored in the output filter (F) can be reduced, also by the ratio of the frequencies. This not only reduces the size and weight of the elements of the filter but also reduces the energy delivered to a "hard arc" should one occur during processing. The third advantage is speed of response. The switch element (S) not only creates an alternating waveform but also controls the amount of power that reaches the output. Since it is operating at a high frequency, it can be controlled at a high frequency, making switchmode power supplies much more agile than their thyristor counterparts. In most designs output power is determined by the percentage of time the switch element (S) is turned on out of each cycle. Also, unlike thyristors, the switches usually used in switchmode power supplies can be turned off in the middle of a cycle, generally within a fraction of a microsecond. This fact, coupled with the low stored energy in the output filter (F), greatly reduces damage to the system or to growing film under arcing conditions.

Arc Control

Should a short appear across the output of the power supply, the entire output voltage will appear across (L) and the inductor in filter (F). This causes the current in these elements to ramp up linearly with time. A current transformer (CT) senses this current rise on the primary side of (T) and, before the current reaches a level that would be dangerous for the switches, turns them off, stopping the current. This sequence

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of events also occurs for arcs, which act like short circuits on the output of the supply (to speed up arc detection and thus reduce the energy delivered to the arc, the current sense circuitry is often additionally programmed to detect a significant change from the nominal current). The so-called "hard arcs," arcs occurring between the sputtering target and earthed points in the system, can be sustained by thermionic emission of small spots within the system, and to ensure the arc does not reinitiate, the power supply must be left off long enough for the emission to reduce below a critical threshold. Much less than 0.1% of all arcs are of this type, however, and if every arc was controlled in this way, process throughput would be reduced because the power supply would be off for a significant fraction of the time.

To address this issue, an arc control inductor (L) is added in series with the output. When an arc occurs, this inductor is effectively placed in parallel with the capacitor in filter (F), with which it forms a resonant circuit. Provided the element values are properly chosen, during an arc, the current in this inductor will ring in a sinusoid and after one-half cycle will attempt to reverse. Most arcs are unipolar; that is, they have a definite cathode and cannot be sustained under conditions of reversing current. These arcs are extinguished by the reversing current long before the primary current of transformer (T) reaches the critical value sensed by the current transformer (CT) to turn off the switches. This simple circuit thereby extinguishes almost every arc in a few microseconds, long before the current can rise in the transformer primary. It is important to note that for this reason, a count of the number of turn-off cycles reported by the power supply logic circuits will not include these automaticallyextinguished arcs. Many power supplies therefore include special arc-detect circuits for arc-counting purposes.

Energy Delivered to Arcs by the Supply

The energy delivered by the power supply to such automatically-extinguished arcs is small, generally less than 20 millijoules. To ensure that unipolar arcs are extinguished by the arc control inductor, however, the element values must be chosen such that the current will indeed reverse. This requires that the peak current delivered from the power supply during the ringing process be many times the sputtering current. Some processes are sensitive to peak current as well as energy delivered and in these cases a modification of the power supply can be made to improve yields at the expense of throughput.

The energy delivered to a "hard arc" is determined by several factors. First, the energy stored in the output filter (F) must be dissipated by the arc, as there is no other path for it. Second, there may be energy stored on the primary side of the transformer (T) that finds its way to the arc. Third, any delay in recognition of the arc by the logic circuits will delay the opening

of the switch element (S) and energy will flow from the mains to the arc through the power supply circuitry. This is called "let-through" energy. For a typical design, the total energy delivered to a "hard arc" will be between 100 and 800 millijoules at an output power of 10 kW, and correspondingly less at lower powers.

For processes sensitive to hard-arc energy, this value can be lowered by increasing the sensitivity of the logic circuits to detection of an arc, thereby shortening the delay in detection of an arc and reducing "let-through" energy. Alternatively, the values of the elements of output filter (F) can be reduced, increasing ripple but lowering the energy stored there; as many processes are not particularly sensitive to ripple and may actually be helped by the presence of high frequency alternating voltage, this can sometimes be a good strategy. Active devices can be placed at the output of a power supply to open the circuit connection to an arc when one is detected or to shunt the energy away from an arc. These devices can reduce the energy delivered to an arc to the low millijoule level, but of course also increase complexity and cost. To address this, alternative design approaches to that represented by Figure 1 are being developed that store only a few millijoules at 10 kW. However, these are just emerging at the time of writing.

Problems in reactive sputtering

Reactive sputtering of insulators using dc power alone can present difficulties with arc control. As reactions occur at the target surface, insulating layers are formed there that charge up due to ion bombardment. The resulting electric fields inside the layers can easily exceed the dielectric strength of the material and breakdown can then occur^[1]. This breakdown generally causes an arc to which the power supply must respond.

To achieve stoichiometric films, the gas flow must be near a critical value that can result in poisoning of the target surface; only the presence of the sputtering power is then keeping the sputtering region of the target metallic. If the power supply turns off for an arc, this metal region of the target will quickly poison and the process will go out of control due to the hysteretic nature of reactive sputtering ^[2]. A number of approaches have been developed in an attempt to overcome this problem, most based upon gas separation ^[3,4], but with limited success. For this reason it is difficult to use dc power alone to sputter insulators such as metal oxides, and another approach must be sought.

QUASI-DC SPUTTERING: PREVENTING ARCING

The above-mentioned difficulties have been classically avoided by the use of radio-frequency power on the target surface. Electrons are attracted to the target surface on the positive peak of every RF cycle and these discharge any insulating regions formed there, preventing buildup of charge to

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the destructive level. Radio-frequency power is very expensive to produce, however, and is difficult to deliver uniformly to large target areas. The required matching networks are expensive and absorb power. In addition, substrate heating can be a problem. For these reasons, this approach has not found use outside of a few specialized applications and in laboratory experiments.

Pulsed DC approaches

For the thin insulating layers formed on the target during reactive sputtering, however, there is no need to resort to radio-frequency power. Depending upon the dielectric constant of the reaction product and the current density of the arriving ions, the layers can be kept discharged with relatively low frequencies. If the layers are kept discharged, arcing can be prevented altogether. For Al_2O_3 , a discharge rate of only 20 kHz is sufficient to prevent dielectric breakdown for current densities of up to 103 A/m³, and it can be shown that the rate required to prevent breakdown is not dependent upon the film thickness ^[5]. This fact has been taken advantage of in the use of a number of approaches to reactive sputtering.

Some workers have used "choppers" or "modulators" to remove the dc from the target periodically ^[6,7]. The circuitry used effectively short-circuits the power supply periodically; this causes the built-up charge to raise the surface potential of insulating regions of the target to positive values, and electrons attracted from the plasma discharge the surface. As the surface is discharged, the potential attracting the electrons decreases, and complete discharge of the surface is not achieved. Some "unipolar pulsed dc" supplies based upon a slightly different principle are available commercially; these contain a series switch that periodically disconnects the supply from the plasma. These are not so useful for reactive sputtering because discharge of the target is obtained only through the mechanism of self-discharge of the layers, which is too slow to be of practical use in this arc-prevention context ^[8].

Considerable success has been achieved by an approach that forcibly reverses the target voltage to a few tens of volts higher than the plasma potential ^[5,9]. This device, Advanced Energy's Sparc-le[®] unit, for which patents are pending, has a basic schematic diagram as shown in Figure 2 on page 6.

When the switch element (S) is open, the Sparc-le[®] unit acts as a simple series inductance. The energy stored in the magnetic field of the inductor acts to steady the current into the plasma. Periodically (the rate can be varied from 2 to 50 kHz) a signal is sent to the switch to close. When the switch is closed, the circuit is changed to that shown in Figure 3 on page 6. The tapped inductor becomes a transformer with a ratio adjustable from 20:1 to 4:1 (some models are not adjustable; these are preset at 8:1). Note that the transformer polarity is such that the voltage is reversed at the output, so the output when the switch is pulsed is positive and varies from 5% to 25% of the nominal sputtering voltage. The pulse width of some models is fixed at 5 or 10 m; in others the pulse width can be adjustable from 1 to 20 m. The voltage waveform for a fixed unit is shown in Figure 4 on page 7.

Meanwhile, an arc detect circuit, (D), sends a signal to close the switch when an arc is sensed. This has the effect of removing the electrons from the arc and quenching it. The voltage waveform for this case is shown in Figure 5 on page 7. Should a hard arc occur that is not quenched by the voltage reversal, some models will leave the switch closed to shunt the system's stored energy away from the plasma. Provision can be made to trigger the arc-detect circuit remotely so that in systems with multiple Sparc-le[®] units, all will act together. This is important because otherwise the triggered unit will act as an anode for the other, still-operating, cathodes, and the resulting current can be quite high in some circumstances.

Workers have been quite successful using these devices to create stoichiometric films of Al_2O_3 , TiO_2 , Ta_2O_5 , and the oxides, nitrides, and carbides of these and Hf, Nb, Cr, Mo, Zr, and Vanadium ^[10,11,12].

"Bipolar pulsed dc" supplies are also available that contain reversal-switching for a dc supply. These units apply the full output voltage of the dc portion of the power supply to the plasma, in either a positive or negative polarity. The positive and negative pulse widths are adjustable over a considerable range (from a few ms up to $\frac{1}{2}$ s) and variable off-times are available between the pulses. Provided the positive pulse is kept short enough to avoid transport of the ions in the plasma to the chamber walls, such a unit can be used for quasi-dc sputtering. Disadvantages of currently available commercial units include availability of voltage regulation only, large physical size, and high cost.

Mixed-Mode Approaches

Low- or medium-frequency ac can be added to dc power to achieve arc-free performance in reactive-sputtering applications ^[13]. In this approach, a "combiner" unit permits connection of an ac generator in the frequency range of 40 to 400 kHz and a dc power supply to the same target. The combiner presents a dc block to the ac generator and an ac block to the dc power supply using series- and parallelresonant circuits, respectively. Carbon films sputtered using this approach have been shown to have more consistent friction characteristics than carbon films sputtered using dc alone. The carbon targets also showed slower growth of the hard regions called "nodules" when mixed-mode power was applied. Silicon dioxide has been reactively sputtered using this approach and compared with films made by dc alone. Optically clear coatings

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were examined using a Nomarski microscope; total integrated scattering at 633 nm was 220 x 10^4 (2.2%) for the dc-sputtered films, but only 3.0×10^4 (0.03%) for mixed-mode films, indicating the much lower number of inclusions and defects in the latter.

Mixed-mode sputtering also showed promise in the reactive O_2 sputtering of alloys in which the metallic constituents oxidize at different rates, and in sputtering Indium-Tin Oxide from the ceramic target. Investigations of ITO films produced from a metallic target showed no loss of film quality using mixed-mode sputtering. Generally, however, while the mixed-mode approach may be advantageous in some processes, it has not been investigated thoroughly because of the ease and lower cost of alternate approaches.

Arc Control

Arc control is more difficult in ac systems and particularly difficult in mixed-mode. Arc detection in ac power supplies varies from rudimentary circuits that merely detect the average voltage to sophisticated circuitry that compares the current on each cycle with the average of the past few cycles; the latter can, of course, act much more quickly. The fastest circuits can shut down the supply within a single ac cycle, greatly limiting the energy delivered into an arc. Mixed-mode systems are more difficult because shut-down of the two supplies must be synchronized.

THE DISAPPEARING ANODE

Any single-target system sputtering an insulator suffers from what can be a serious problem: the current return path to the power supply can disappear. In conventional dc magnetron sputtering, an electron trap is formed over the cathode surface and an intense plasma is formed there from which ions are drawn to sputter the target surface. Withdrawal of ions from the plasma changes the potential there and causes electrons to "leak" from the plasma; these electrons are attracted to the anode of the system (the element to which the positive lead of the power supply is attached—often this is simply the chamber walls) and form the return-current to the power supply.

When the growing film is an insulator, every surface of the chamber will eventually be coated by insulating compounds and there will be no path for the electrons to return to the power supply. The effect from the power supply's point of view is that the impedance of the load begins to rise; this causes the voltage to increase, and eventually the power supply will go out of regulation. Inside the chamber, the plasma becomes diffuse and eventually extinguishes. Even before this happens, the coating of the anode structure can cause serious nonuniformity in the plasma and in the deposition rates in large-area coaters. While this problem may be only a minor nuisance in a laboratory or small-scale environment, it can be a major issue in systems scaled up to industrial production. A number of approaches have been tried to eliminate or ameliorate this problem, including anodes placed out of sight of the discharge, rotating anodes, wire-fed anodes, and anodes using magnetic fields to bend the electrons into a re-entrant structure. In many cases, simple maintenance involving replacement of removable elements in the system have proved adequate, but for very large-scale production of highly insulating films, a clever method using two cathodes shows promise.

LF AND DUAL-CATHODE SPUTTERING

In the late 1970s, a group headed by Robert Cormia at Airco investigated low-frequency ac reactive magnetron sputtering and was granted a patent on the technique ^[14]. Their system used a single magnetron; an alternating voltage with frequencies from 60 Hz to some tens of kilohertz was applied to the target. Sputtering TiO, and using 10 kHz power, they reported no arcing under any conditions. This single-target system suffers, however, from a disadvantage related to the "disappearing anode" problem outlined above. Once the chamber is covered with insulating material, there can be no average (dc) current flowing in the power supply leads. This means that a plasma must be formed on every half-cycle of the ac waveform, even when the target is positive. Since Cormia used a conventional anode in his experiments, the plasma had to be ignited in the diode mode (nonmagnetically-enhanced), which caused sputtering of the anode and contamination of the film. This lead to the suggestion that the counter-electrode be a magnetron target and the invention of the dual-cathode system. First described by G. Este at BNL [15], this concept was developed by several investigators simultaneously ^[16,17]. In this approach, an ac power supply is connected between two cathodes; each acts as an anode for the other during alternate half cycles of the ac waveform. The considerable advantage offered by the dual-cathode approach is the solution to the disappearing anode problem, since the anode on each half-cycle is a freshly-sputtered surface and is therefore guaranteed to be clean.

SINUSOIDAL SYSTEMS

In the simplest approach, the ac power supply consists of a sinusoidal generator. Idealized waveforms appearing at the cathodes for this case are shown in Figure 6 on page 7. Electrons arriving at elements being driven positive clamp the voltage there to the plasma potential, and the full voltage therefore appears at the element being driven negative. It should be obvious that the targets must "see" each other (be in short line of sight) for the electrons to be able to arrive at the positive target and complete the electrical circuit. This prevents

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